THE MECHANISM OF THE CATALYTIC CRACKING OF UNSYMMETRICAL DIARYLETHANES

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The catalytic cracking of substituted 1 : 1-diarylethanes on siliceous catalysts to form a substituted styrene was studied as a function of temperature, contact time, diluent, catalyst particle size and area. At suitable low contact times of 0·001-0·1 sec. at 500° C the reaction is essentially without side reactions, hence is ideal for cracking studies. The reaction has a low temperature coefficient. In contrast with most catalytic reactions the rate of cracking is dependent on the number of collisions of the diarylethane with the *external* area of the catalyst particles and on this basis the variables affecting the rate are correlated. The true internal surface area is not an important factor in the cracking rate.

The rate of cracking decreases as the electronegativity of the substituents increases and the order observed for this effect is apparently the same as in Hammett's *reactivity series*. Because of this correlation it appears that a carbonium ion mechanism is involved in this fast reaction. About one collision in every thousand with the catalyst surface is effective and it is suggested that during an effective collision the consecutive steps in the carbonium ion mechanism take place essentially simultaneously.

It has not been possible for earlier investigators to work out many of the details of the kinetics of hydrocarbon cracking reactions because of the complexity of the mechanism and the products formed by cracking. The catalytic cracking on siliceous catalysts of 1 : 1-*bis* (4-methylphenyl)-ethane (referred to as ditolylethane), a compound which is a typical example of an unsymmetrical diarylethane, forms methylstyrene and toluene with but little tendency to yield numerous or complex by-products. Therefore, this type of reaction has proven to be suitable for a quantitative study of a number of variables affecting the kinetics.

The cracking of substituted unsymmetrical diarylethanes to form a substituted styrene and the aromatic hydrocarbon was discovered and investigated by Sturrock and Lawe.[1] These two workers initially pointed out and interested us in the unique features of this cracking reaction and have co-operated in the development of the studies reported herein. Their work and the later report of Morton and Nicholls [2] indicated the nature of certain variables affecting the cracking rate without relating these factors in the more quantitative manner described in this paper. Greensfelder, Voge and Good have published an important series of papers [3] on the cracking of pure hydrocarbons, and Thomas [4] has recently presented a theory of the mechanism, which will be of importance in discussing the results of this paper.

Experimental

Materials.—The 1 : 1-*bis* (substituted phenylethanes) were usually prepared by condensation of acetylene or acetaldehyde with a substituted aromatic compound in the presence of a Friedel-Craft's catalyst such as aluminium chloride and anhydrous hydrofluoric acid, zinc chloride, etc. For example, 1 : 1-*bis*-(4-methylphenylethane) was synthesized by condensation of toluene with acetaldehyde using a 3-5-fold molar excess of the hydrocarbon at 0-5° C with anhydrous hydrofluoric acid as catalyst.

Cracking Procedure and Analyses.—The cracking of the diarylethane was carried out in conventional equipment. The liquid diarylethane was metered and flash-vapourized. The vapour was mixed with a metered flow of steam and the resulting mixture passed through an electrically heated stainless steel tube maintained at a controlled temperature. The products were quenched and the water layer separated. The off-gas was always negligible. The catalyst decreased in activity during each run but could be restored to the original activity by " burning off " with air in the presence of steam.

The oil layer from the products was stripped at reduced pressures to obtain low boilers. In the case of ditolylethane, for example, these consisted of toluene, ethyltoluene, and methylstyrene. In most cases only 0·1-5 % of the substituted styrene was recovered with the vinyl group in the hydrogenated state. Probably this side reaction occurs by hydrogen transfer from the tar on the catalyst to the vinyl group. The moles of methylstyrene plus ethyl derivative is, however, an accurate measure of the total cracking of the diarylethane.

Extensive distillation or crystallization work, carried out with the aid of infra-red analyses, led to preparation of pure substituted styrenes and the ethyl derivatives. This permitted setting up of quantitative infra-red analytical procedures for the multi-components in the low boilers from the cracking. Samples were adequately analyzed by use of a combination of infra-red, bromide-bromate titration for substituted styrene, and distillation.

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[1] Sturrock and Lawe, *U.S. Pat.* 2,373,982, April 17, 1945, to the Dominion Tar and Chemical Company.

[2] Morton and Nicholls, *Can. J. Res. B*, 1948, **26**, 581.

[3] Greensfelder, Voge and Good, *Ind. Eng. Chem.*, 1949, **41**, 2573.

[4] Thomas, *ibid.*, 1949, **41**, 2564.

Pellets made from Merck's kaolin were used as catalyst. This clay had a surface area as measured by the low temperature nitrogen adsorption of around 10 m.²/g. It contained 44 % SiO_2, 42 % Al_2O_3, and 14 % H_2O. A highly active commercial petroleum cracking catalyst containing 90 % SiO_2-10 % Al_2O_3, surface area 500 m.²/g., was also employed.

Results

The rate of cracking of ditolylethane was studied as a function of the contact time, temperature, molar ratio of steam as diluent to ditolyethane, and the diameter of the kaolin catalyst pellets. After reactivation of the kaolin the rate was determined as a function of the time of operation from which the value at zero time was found by extrapolation. Table I summarizes the data obtained.

TABLE I—CATALYTIC CRACKING OF 1 : 1-DI-*p*-TOLYLETHANE, DILUTED WITH STEAM, OVER A KAOLIN CATALYST AT 525° C

(Pressure 1·1 ± 0·1 atm.)

Run No.	Catalyst Particle Diameter cm.	Catalyst Volume, V_a in cm.³	Contact Time, V_a/V, sec.	Collision Frequency Factor, X	% Cracked to Low Boiling Fraction		% Ethyl-toluene Based on Methyl-styrene
					Extrapol-ated to Start	For 2 g. per cm.³ Passed Catalyst	
10/1 mole Dilution of Steam to 1:1-Di-*p*-tolylethane							
42	0·20	15	0·014	0·07	29	27	0·9
40-2	0·062	6	0·0064	0·12	50	47	0·2
39-3	0·11	15	0·015	0·16	56	53	0·4
34	0·20	60	0·067	0·36	61	58	1·6
43	0·11	60	0·088	1·1	68	64	2·3
132	0·11	100	0·50	5·6	—	62	16
126	0·11	100	0·86	8·1	—	44	40
127	0·11	100	2·0	19	—	30	60
100/1 mole Dilution of Steam to 1 : 1-Di-*p*-tolylethane							
37	0·11	6	0·0064	0·06	30	28	0·0
41	0·20	15	0·016	0·08	34	32	0·4
40-1	0·062	6	0·0066	0·12	51	48	0·2
39-1	0·11	15	0·017	0·17	65	62	0·0
35	0·20	60	0·067	0·35	78	76	0·0
38	0·062	15	0·024	0·48	82	78	0·0
44	0·11	60	0·083	0·93	92	87	0·8
122	0·11	67	0·13	1·3	—	84	6·3
129	0·11	100	0·56	6·6	—	85	*15

* The ditolylethane passed was 1·0 g. cm.⁻³ catalyst. Therefore, this value is high.

The contact time is calculated for the average pressure over the catalyst in atmospheres, and at the reaction temperatures. The collision frequency factor in column 5 will be explained below. The percentages of ditolylethane converted to methylstyrene and ethyltoluene are shown in columns 6 and 7 at the start of the run and after passing 2 g. cm.$^{-3}$ catalyst. The last column shows a negligible formation of ethyltoluene up to 60-90 % conversion.

Experiments in Table I show that if only one factor (contact time, particle size and dilution) is varied at a time, then the converson increases with contact time, dilution and smaller particle size. These variables affecting the conversion are best related by means of the kinetic analysis presented below.

It was observed that the conversion was the same for solid pellets of kaolin as on a non-porous carborundum carrier coated with 16 % kaolin containing 2 % sodium silicate. In a private communication Dr. M. G. Sturrock has informed us that the weight of kaolin on the carrier need be only some 5-10 % in order to achieve the same conversion, yields, etc., as were obtained with the solid kaolin, and any further increase in coating over 10 % had no effect. This indicated that the external (geometrical) area of the pellets and not the true internal surface area, was the important factor. This suggested that the number of collisions of the diarylethane with the external area was important and explained the observed effect that a decrease in catalyst particle diameter increased the conversion.

If we assume that the rate of cracking over any element of length of the catalyst is dn mole/sec., and that the rate is dependent on the number of collisions with the external area of the catalyst, then

$$dn = -kZdS, \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where Z = number of collisions per sec. and dS the external area of catalyst in the element under consideration. At the high dilutions of steam used here the change in volume on reaction may be neglected and the pressure P is essentially constant at one atmosphere. Z is proportional to the partial pressure of diarylethane, which is nP/V, where V = initial volume space velocity of vapour passing over the catalyst in cm.^{3}/sec. This volume includes the steam added as diluent. The external area of the catalyst is $S = k_2V_a/d$, where k_2 = constant, V_a the volume of catalyst and d = particle diameter. By integration

$$\ln n/n_0 = -k_1X, \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where X, the collision frequency factor, is V_aP/Vd, and n_0 is the number of moles/sec. of diarylethane fed.

Values of the collision frequency calculated in this way are given in Table I and are plotted in Fig. 1 against the logarithm of the fraction unconverted.

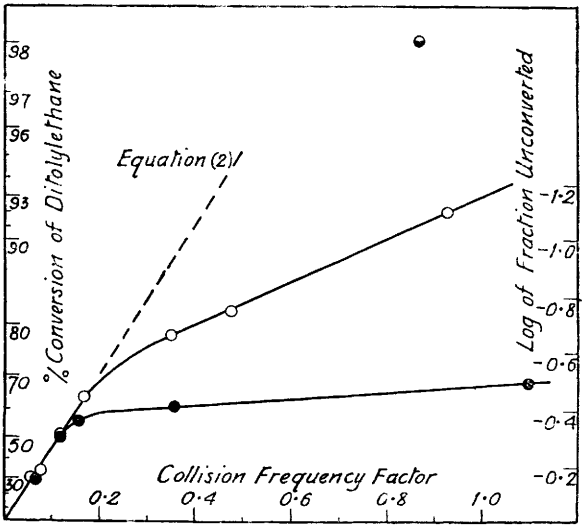


FIG. 1.—Conversion of Ditolylethane against collision frequency factor.
● Dilution, 10/1. ○ Dilution, 100/1. ◒ Dilution, 265/1.

The resulting curve should by eqn. (2) be a straight line. The correlation of the three variables involved in the collision frequency is reasonably good. With a high collision frequency factor the observed conversion is lower than predicted presumably because of an approach to an equilibrium or to a dependence on diffusion which lowers the conversion and makes the extrapolation to zero time less accurate.

Temperature Coefficient.—The conversion of ditolylethane to methylstyrene was determined at several temperatures under comparable conditions on kaolin catalyst. Conversion was obtained at the start of the run and after 10 g. of ditolylethane had been passed per g. of catalyst. The results are shown in Fig. 2, from which it is calculated that the apparent activation energy is 5000 cal./mole.

Effect of Substituents on Cracking Rate.—Using the relation

$$\log n/n_0 = -k_1X,$$

the ratio of collision frequency factor for any substituted diarylethane to that for ditolylethane, at equal values of conversion, gives the ratio of velocity

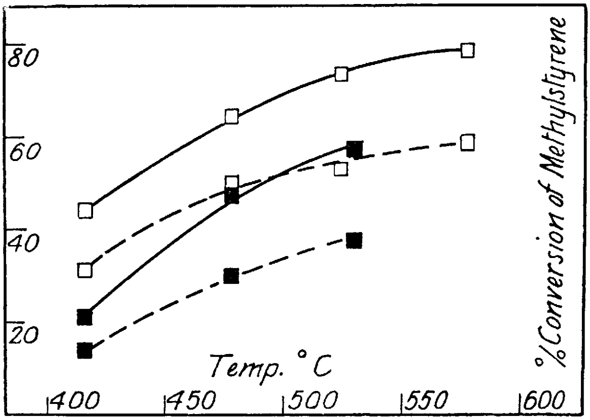


Fig. 2.—Variation in the conversion of 1 : 1-di-*p*-tolylethane to *p*-methylstyrene with temperature of pyrolysis.

Full lines : Conversion at start. Broken lines : conversion at 10 g. ditolylethane passed per g. catalyst.

Contact time : 0·08 sec. Catalyst pellet size : 0·203 cm.

Molar dilutions of ditolylethane vapour.

■ Dilution, 10. □ Dilution, 100.

constants k_1. In some cases the velocity constants were estimated from limited data, but the approximation involved would not change the order of effectiveness of substituent groups. Table II summarizes data for kaolin pellets, and for the petroleum cracking catalyst containing 90 % SiO_2-10 % Al_2O_3.

It is evident from Table II that an increase in electronegativity of the substituent in the nucleus of the diarylethane decreases the rate of cracking.

TABLE II—Relative Rate Constants of Substituted Diarylethanes using Kaolin and 90 % Silica–10 % Alumina Catalysts

Substance (a)	Relative Rate Constant on (b)	
	Kaolin	SiO_2–Al_2O_3
1 : 1-*bis* (4-Hydroxyphenyl)ethane	(< 5)*	—
2 : 2-*bis* (4-Aminophenyl)propane	(< 5)*	—
1 : 1-*bis* (2 : 4-Dimethylphenyl)ethane	1·4	3·8
1 : 1-*bis* (4-Methylphenyl)ethane	1·0	4·2
1 : 1-*bis* (2-Thienyl)ethane	(1)*	—
1 : 1-*bis* (4-Aminophenyl)ethane	(1)*	—
1 : 1-*bis* (4-Dimethylaminophenyl)ethane	(1)*	—
2 : 2-*bis* (4-Hydroxyphenyl)propane	(1)*	—
1 : 1-*bis* (2-Naphthyl)ethane	0·5	—
1 : 1-Diphenylethane	0·3	1·0
1 : 1-*bis* (4-Chlorophenyl)ethane	0·04	0·5
1 : 1-*bis* (3 : 4-Dichlorophenyl)ethane	0·01	0·2
1 : 1-*bis* (2 : 5-Dichlorophenyl)ethane	—	0·1
1 : 1-*bis* (4-Cyanophenyl)ethane	Very small	0·05*

(*a*) Structure essentially as designated. In some cases, isomers were present.
(*b*) Ditolylethane over kaolin is the reference standard.
* Only estimated from limited data.

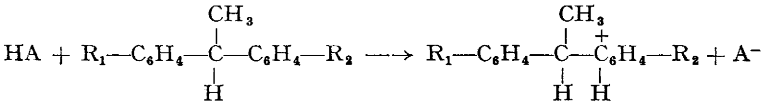
The relative order shown is in qualitative agreement with that given by Hammett [5] in his reactivity series. A mixed diarylethane containing no sub-

[5] Hammett, *Physical Organic Chemistry* (McGraw-Hill Book Co., 1940), Chap. 7.

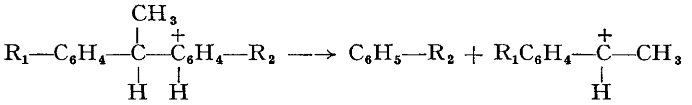
stituents on one ring and chlorine on the other, i.e. 1-phenyl-1-(chlorophenyl)-ethane was synthesized and cracked. The resulting styrenes contained chlorostyrene and styrene in mole ratio of 4/1, thus again indicating an increase in electronegativity decreases the tendency of the bond between phenyl ring and the ethanoid carbon to crack. These results indicate an ionic type and more specifically a carbonium ion mechanism is involved in the cracking of these diarylethanes.

Discussion

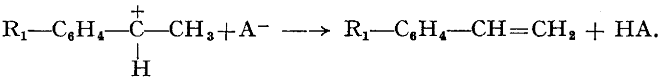
Mechanism of Cracking Reaction.—The mechanism of the cracking of hydrocarbons on alumina-silica catalysts has been described in a recent paper by Thomas[4] and also by Greensfelder, Voge and Good.[3] They represent siliceous cracking catalysts as acids which are capable of donating their protons to the hydrocarbon, thus forming a carbonium ion which then rearranges or decomposes to form the products of the cracking reaction. If we apply the above concepts to the cracking of substituted diarylethanes, and represent the catalyst by HA, then the equations for reaction are as follows :



$$HA + R_1{-}C_6H_4{-}\overset{CH_3}{\underset{H}{C}}{-}C_6H_4{-}R_2 \longrightarrow R_1{-}C_6H_4{-}\overset{CH_3}{\underset{H}{C}}{-}\overset{+}{\underset{H}{C}}_6H_4{-}R_2 + A^- \quad (3)$$



$$R_1{-}C_6H_4{-}\overset{CH_3}{\underset{H}{C}}{-}\overset{+}{\underset{H}{C}}_6H_4{-}R_2 \longrightarrow C_6H_5{-}R_2 + R_1C_6H_4{-}\overset{+}{\underset{H}{C}}{-}CH_3 \quad (4)$$



$$R_1{-}C_6H_4{-}\overset{+}{\underset{H}{C}}{-}CH_3 + A^- \longrightarrow R_1{-}C_6H_4{-}CH{=}CH_2 + HA. \quad (5)$$

The catalyst is regenerated and starts the cycle again.

If R_1 and R_2 are the same, and their electronegativity is increased, the tendency to form a carbonium ion in eqn. (3) is decreased and the cracking rate is also decreased because of the increase in positive charge at or near the bond between the ring and the ethanoid group. It is suggested that reactions (3)-(5) take place consecutively but essentially simultaneously, a proton from one part of the catalyst taking part in eqn. (3), and another part of the catalyst accepting the proton liberated in eqn. (5). This concept is analogous to that which has been proposed by Turkevich[6] and by Hansford.[7]

A calculation shows that at zero time the number of collisions of diarylethane with the surface is around 1000 times the experimental number of molecules decomposed. The observed activation energy would account for 40 out of the 1000 and steric factors could easily explain the remainder of the difference. The use of internal rather than external areas in calculating the number of collisions would make the discrepancy considerably larger. Experimental evidence favours the use of external area.

This cracking reaction is unusual because (1) the thousand-fold difference is unusually low for most catalytic reactions, (2) there is no need for requiring activated adsorption of the diarylethane with a prolonged residence time on the surface in order to account for reaction, (3) the external geometric surface of the catalyst is a controlling factor, and (4) the effect of chemical structure on reactivity is predictable.

[6] Turkevich and Smith, *J. Chem. Physics*, 1947, **16**, 466.
[7] Hansford, *Ind. Eng. Chem.*, 1947, **39**, 849.

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